

# Decoherence and surface hopping: When can averaging over initial conditions help capture the effects of wave packet separation?

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Fewest-switches surface hopping (FSSH) is a popular nonadiabatic dynamics method which treats nuclei with classical mechanics and electrons with quantum mechanics. In order to simulate the motion of a wave packet as accurately as possible, standard FSSH requires a stochastic sampling of the trajectories over a distribution of initial conditions corresponding, e.g., to the Wigner distribution of the initial quantum wave packet. Although it is well-known that FSSH does not properly account for decoherence effects, there is some confusion in the literature about whether or not this averaging over a distribution of initial conditions can approximate some of the effects of decoherence. In this paper, we not only show that averaging over initial conditions does not generally account for decoherence, but also *why* it fails to do so. We also show how an apparent improvement in accuracy can be obtained for a fortuitous choice of model problems, even though this improvement is not possible, in general. For a basic set of one-dimensional and two-dimensional examples, we find significantly improved results using our recently introduced augmented FSSH algorithm. © 2011 American Institute of Physics. [doi:10.1063/1.3603448]

## I. INTRODUCTION: FEWEST SWITCHES SURFACE HOPPING (FSSH), DECOHERENCE, AND INITIAL VALUE REPRESENTATIONS

Modeling nonadiabatic dynamics correctly is crucial for understanding electron transfer, electronic excitation transfer, or any form of electronic relaxation.<sup>1</sup> In recent years, the FSSH (Refs. 2 and 3) algorithm has become popular as a simple nonadiabatic tool with two very appealing qualities: (i) FSSH requires that the nuclei always propagate on a particular electronic adiabat, thus allowing FSSH to treat bond making and breaking events where using the correct asymptotic surface is crucial; (ii) FSSH forbids classical nuclei from populating energetically inaccessible electronic states, thereby closing all energetically forbidden channels during inelastic scattering and also approximately enforcing detailed balance.<sup>4</sup>

The most prominent shortcoming of surface-hopping is that FSSH suffers from the problem of “over-coherence.” To understand how this problem arises, recall that surface-hopping requires equations of motion for both classical nuclear motion and (quantum-mechanical) electronic amplitude propagation. There is an important question here as to whether these equations will always be consistent, in the sense that the electronic state and the nuclear forces correspond correctly to each other. The fully quantum-mechanical Schrodinger equation is, of course, automatically consistent between nuclei and electrons, but semiclassical surface-hopping techniques need not be so. In general, for a swarm of trajectories, FSSH finds consistency by forcing stochastic hops between surfaces so as to match the number of trajec-

tories on each surface with the electronic wavefunction. The result is a set of discontinuous classical trajectories and a very reasonable set of populations.

Now, the FSSH algorithm faces a unique obstacle when a classical nucleus enters a region of configuration space where different surfaces feel very different forces. Ideally, the classical nuclei in FSSH should represent heavy, compact quantum nuclear wavefunctions and these wavefunctions can certainly bifurcate into more than one wave packet on different surfaces, as one would find with exact quantum dynamics or multiple-spawning trajectories.<sup>6,7</sup> While this is clearly the correct physical picture, unfortunately, from the perspective of the electronic degrees of freedom, FSSH does not correctly treat this bifurcation of a nuclear wave packet: instead, the electronic wavefunction is still propagated along the instantaneous nuclear trajectory, as if the electronic amplitudes were unaware that the total wave packet is now breaking apart. In the language of the decoherence literature, the components of the electronic wavefunction on different electronic surfaces always remain coherent. This overcoherence can lead to spurious results for long-time dynamics, especially if nuclei visit more than one distinct region of derivative coupling.<sup>5</sup>

Many useful and creative solutions have been proposed in the literature for overcoming this decoherence problem, while retaining a simple trajectory-based algorithm. In order to add decoherence directly and empirically to FSSH, the simplest approach is to enforce stochastic wavefunction collapse, as proposed by Rossky and Prezhdo,<sup>8–14</sup> Schwartz,<sup>15,16</sup> Truhlar,<sup>17–22</sup> Hammes-Schiffer,<sup>23</sup> and co-workers. In other words, just as the nuclear trajectories have discontinuities in the standard FSSH algorithm, one now allows also the electronic wavefunctions to have occasional discontinuities. Beyond standard FSSH trajectories, other algorithms have

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been developed that start from the quantum Liouville equation and derive equations of motion which yield new (stochastic) trajectories for the full nuclear-electronic density matrix.<sup>24–35</sup> Finally, as a very different alternative to the stochastic trajectories above, it is important to note that the Meyer-Miller-Stock-Thoss (MMST) (Refs. 36–38) is a rigorous semiclassical formalism for nonadiabatic dynamics that overcomes the decoherence problem by adding together semiclassical trajectories fully coherently with a semiclassical phase. Interestingly, these semiclassical trajectories are effectively just Ehrenfest trajectories. After integrating over an initial value representation of the wave packet, the MMST approach finds that the decoherence problem vanishes by phase interference.

In trying to analyze the best approach for decoherence and FSSH, there remains a question in the literature as to whether the problem of decoherence in FSSH can be partially addressed simply by sampling trajectories stochastically over a distribution of initial conditions. Logically, a quantum mechanical wave packet has uncertainty in its position and momentum, and semiclassical treatments of wave packets inevitably consider a wave packet to be constructed from a swarm of classical particles with a spread in position and momentum, e.g., a Wigner distribution. On a single potential energy surface, integration over a classical distribution of particles helps describe the “tunneling” of a wave packet  $|\Psi\rangle$  and subsequent wave packet separation and fragmentation (e.g., (Refs. 39 and 40)). Now, since the MMST approach shows rigorously that integrating over such initial value representations with phase is crucial for understanding decoherence, i.e., wave packets separating on different surfaces, one might wonder whether any partial success can be achieved for FSSH simply by averaging over initial conditions, even without phase.

The suggestion that averaging over initial conditions might partially account for elements of decoherence goes back to Tully’s model problem #3 (“extended coupling”) in his seminal article on surface hopping.<sup>2</sup> Consider the model problem (shown in Fig. 1), and imagine a Gaussian wave packet incoming from the left on the lower adiabat. When the wave packet reaches  $x = -6$ , the two adiabatic surfaces are coupled, and thus two wave packets emerge from this region, one on the lower adiabat and one on the upper adiabat. Once the wave packets reach the region  $x > 0$ , they begin to experience very different forces. By this point in time, the surfaces are now barely coupled and the motion of each wave packet is effectively independent from the other. Thus, on the one hand, the wave packet on the lower surface feels a strong force rightward, so that it transmits. On the other hand, the wave packet on the upper surface feels a strong force leftward and, for small enough initial kinetic energy, the wave packet reflects leftward. And as the wave packet reflects, it again crosses the region of derivative coupling between adiabatic surfaces around  $x = -6$ . At this point, the single wave packet should emerge as two new wave packets, one on each adiabatic surface, resulting in nonzero branching ratios for both reflection channels.

Because there are no quantum interferences involved in this process, we would not expect to see any oscillations in these branching ratios as a function of incoming momentum.

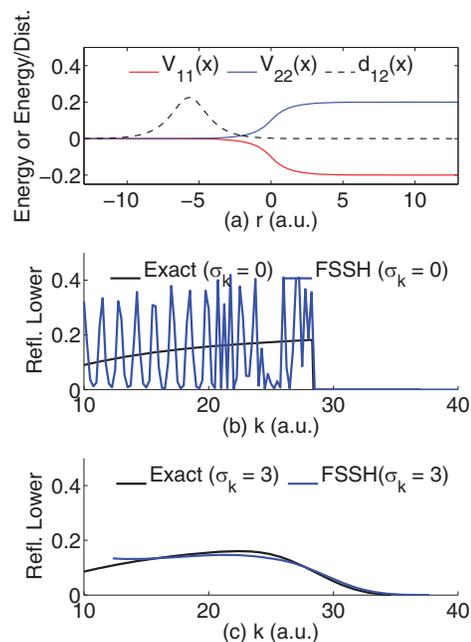


FIG. 1. (a) The adiabatic potential energy surfaces  $V_{11}(x)$  and  $V_{22}(x)$  for Tully problem #3, and the derivative coupling,  $d_{12}(x)$ . (b) Branching ratios for reflection onto the lower surface for either incoming plane waves treated quantum-mechanically (exact) or incoming classical particles with fixed momentum treated with surface hopping (FSSH)—the FSSH results are not averaged over any initial conditions. (c) Branching ratios for quantum wave packets of finite width (exact) or a swarm of classical particles with a spread in initial momentum (FSSH,  $\sigma_k = 3$ ) [Eq. (2)]. Note that, even though FSSH does not match plane wave results, FSSH is much more accurate when averaged over initial conditions to simulate a wave packet’s trajectory. We will show below that this agreement is purely coincidental and is very unlikely, in general, for other, similar Hamiltonians where there are very different forces on different adiabatic surfaces and wave packets may bifurcate.

In practice, however, one finds spurious oscillations in the reflection probabilities of the different channels using the FSSH algorithm, as shown in Fig. 1(b). These oscillations are caused by the fact that FSSH does not properly treat the bifurcation of one wave packet into multiple wave packets moving in different directions (i.e., decoherence). Now, very interestingly, Tully showed that by “averaging the trajectory results over the same spread of momenta embodied in the [quantum mechanical] wave packet... oscillations are almost completely removed, and classical and quantal calculations are thus in complete agreement.”<sup>2</sup> See Fig. 1(c). This observation suggests that there might be a connection between decoherence in condensed phase systems and averaging over a range of initial conditions (see, for instance, Refs. 5 and 41), and the literature does not appear to have any conclusive statements on the precise nature of this connection.

In this paper, our goal is to elucidate the connection between stochastic sampling over initial conditions and decoherence. First, for a set of simple one-dimensional Hamiltonians, we will explore whether any effects of wave packet separation can be modeled by averaging FSSH results over initial conditions. We will show that, while averaging over initial conditions is necessary for modeling the dynamics of a wave packet with finite width, it is not at all sufficient for treating decoherence and it succeeds only in fortuitous cases. Second, to explain the fortuitous results in Fig. 1(c), we will

then show exactly why, in some rare cases, averaging over initial conditions does give the correct answers. Third, by investigating more complicated Hamiltonians, we will establish that our conclusions in this paper generalize to more than one spatial dimension. Fourth and finally, we demonstrate that our recently introduced augmented FSSH algorithm (A-FSSH),<sup>42</sup> treats all of these problems accurately, often allowing us to recover the exact results once we average over initial conditions.

## II. MODEL PROBLEMS AND RESULTS

All model problems below have been tested on a particle with mass = 2000 a.u. All calculations were done in atomic units ( $\hbar = 1$ ), using the Runge-Kutta 4/5 integrator with a time step of  $dt = 0.3$  a.u.

### A. An avoided crossing: Inelastic scattering with resonances

Before we explore the complicated dynamics in Fig. 1, we first model the simplest nonadiabatic problem, an avoided crossing. Tully himself also studied an avoided crossing in Ref. 2, but, for reasons to be explained shortly, we have chosen a slightly different Hamiltonian with a smaller diabatic coupling so that our adiabatic surfaces display a narrower avoided crossing. The Hamiltonian in Eq. (1) (which is plotted in Fig. 2(a)) demonstrates why, in general, we must average FSSH results over initial conditions in order to simulate wave packet dynamics:

$$\begin{aligned} V_{11}(x) &= A \tanh(B(x+7)), & A &= 0.03, \\ V_{22}(x) &= -A \tanh(B(x+7)), & B &= 1.6, \\ V_{12}(x) &= C e^{-(x+7)^2}, & C &= 0.005. \end{aligned} \quad (1)$$

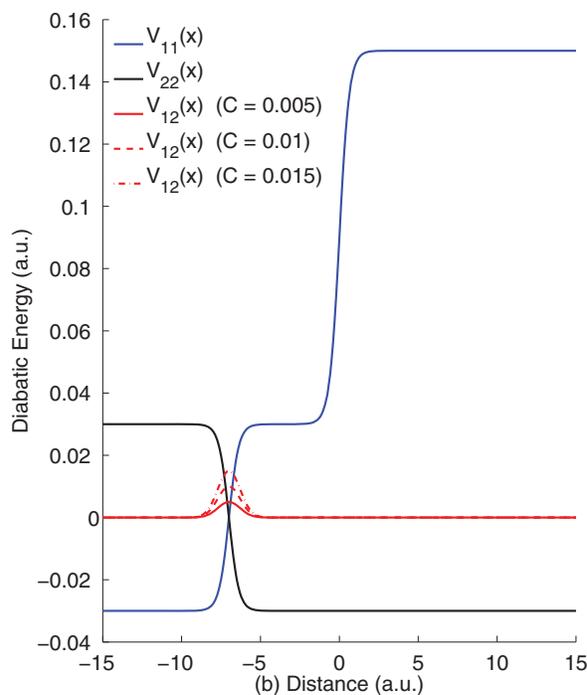
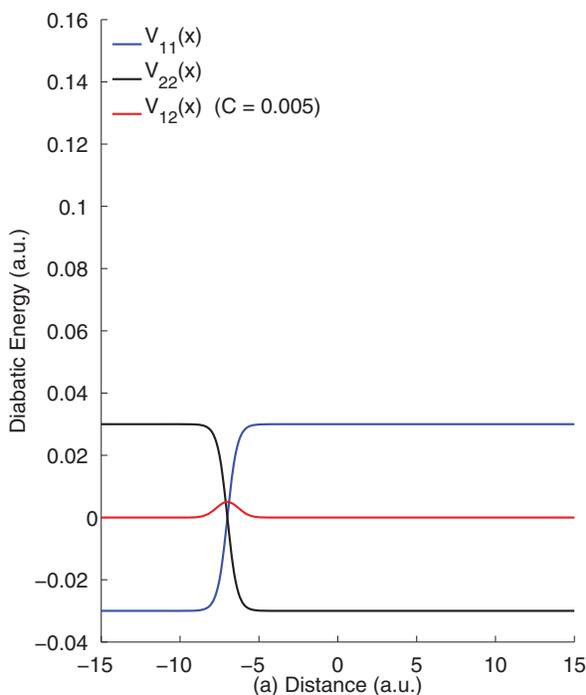


FIG. 2. The diabatic potential energy surfaces for (a) an avoided crossing, Eq. (1); and (b) an avoided crossing with reflection, Eq. (3).

In Fig. 3, we show results. We imagine a particle incoming on the lower adiabatic surface from the left in Fig. 2(a). In Fig. 3(a), we plot the probability of reflection on the lower surface as a function of incoming wavevector ( $k_{inc}$ ) for an infinitely broad wave packet, i.e., a plane wave with  $\sigma_k = 0$  (denoted “ $w_{scatt}$ ”). In Figs. 3(b) and 3(c), we plot results for Gaussians with width  $\sigma_k = 0.25$  and  $\sigma_k = 0.5$ , which can be obtained according to

$$w_{Gauss}(k) = \frac{1}{\sqrt{2\pi\sigma_k^2}} \int dk' \exp\left(-\frac{(k'-k)^2}{2\sigma_k^2}\right) w_{scatt}(k'). \quad (2)$$

There are four distinct energetic domains in Fig. 3. (i) For  $k_{inc} > 15.75$ , we find only transmission and no reflection at such high energies. The more interesting regions are for  $k_{inc} < 15.75$ , where the upper state is closed and we find only transmission and reflection onto the lower channel. Especially important is region (ii),  $12 < k_{inc} < 15.75$ , where the particle hops between upper and lower adiabatic surfaces, but cannot emerge on the upper surface. This trapping region exists also in Tully’s avoided model problem,<sup>2</sup> but it is much broader in our case because we have chosen a smaller diabatic coupling. In region (iii), for  $k_{inc} < 12$ , the particle never has enough kinetic energy to hop up onto the upper surface, but the particle does not have enough energy to overcome the barrier on the lower surface, so that we find only transmission on the lower surface. Finally, (iv), for  $k_{inc} < 10$  or so, the particle cannot overcome the barrier on the lower adiabatic surface and can only reflect.

From Fig. 3, we see clearly that in order to best match quantum wave packet results, we must average FSSH results over the corresponding distribution of initial conditions. In

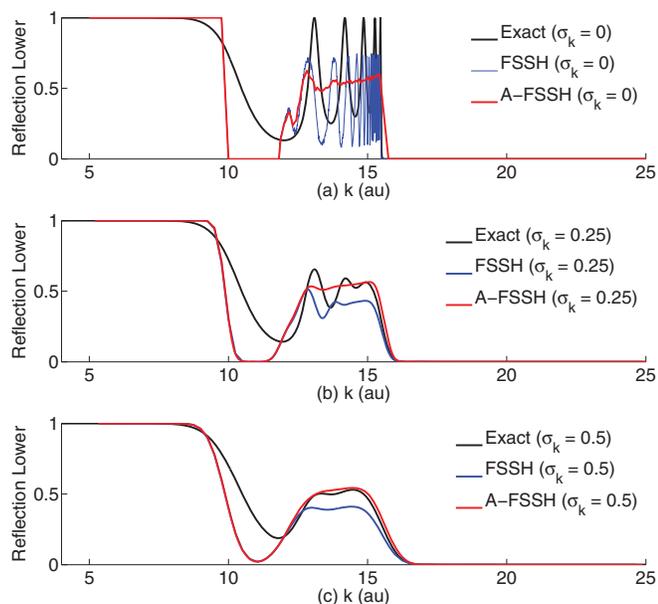


FIG. 3. Probabilities for reflection on the lower surface for an avoided crossing, Eq. (1). The potential energy surfaces are shown in Fig. 2(a) and we imagine the particle incoming on the lower adiabatic surface from the left. (a) Plane wave quantum calculations and raw FSSH data starting from one initial momentum. [(b), (c)] The same branching ratios for quantum wave packets and FSSH data averaged over the corresponding spread in initial conditions. This data demonstrates empirically why averaging over initial distributions is essential for a correct interpretation of FSSH results. Note that our recently developed A-FSSH algorithm, with a decoherence correction, ignores some of the oscillations in the exact branching ratios for a plane wave but recovers the correct reflection probability for a compact (classical) wave packet.

Fig. 3(a), the five sharp peaks in reflection for an incoming plane wave signify quantum resonances, where we imagine the particle spending some finite time trapped in the upper electronic state; FSSH cannot match these results even qualitatively – FSSH predicts more than 10 resonance peaks. This result is perhaps not surprising since one should not expect FSSH to recover branching ratios for infinitely wide wave packets, where classical mechanics is surely inadequate. Nevertheless, after averaging over initial conditions, FSSH results show much greater agreement with wave packet results.

From this picture, there is no doubt that the best quantum mechanical interpretation of FSSH trajectories requires averaging over initial conditions. Because the plane wave results are oscillatory, the wave packet calculations will be smoothed out depending on the initial width of the quantum wave packet. Therefore, the FSSH results also ought to depend on the width of the initial distribution. Because each FSSH trajectory depends sensitively on its initial conditions, one must average over the initial conditions to match the exact dynamics of the corresponding quantum wave packet. Encouragingly, Fig. 3 shows that for reasonably compact wave packets, FSSH is able to capture many of the correct features, at least qualitatively. Just as averaging over initial conditions is necessary for calculating “above-the-barrier tunneling” and the branching of a quantum wave packet into reflected and transmitted components on even a single surface, such averaging is also necessary for calculating branching ratios in this nonadiabatic problem. Nevertheless, even with stochastic sampling we find here that the FSSH results are not quantita-

tively accurate and the reasons behind this discrepancy are unclear. To better identify the source of the surface hopping failures described above, we will now switch to a model problem without any oscillations in the plane wave results (i.e., without quantum resonances), so that we can distinguish between the problems associated with the presence of resonances and the problems associated with decoherence.

## B. Electron relaxation without resonances

To better understand the origins of surface hopping’s failures and the limitations of averaging over initial conditions, consider the diabatic Hamiltonian in Eq. (3) (plotted in Fig. 2(b)), (which roughly represents Tully’s model problem in Fig. 1):

$$\begin{aligned} V_{11}(x) &= 2A \tanh(Bx) + A \tanh(B(x+7)) + 2A, \\ V_{22}(x) &= -A \tanh(B(x+7)), \\ V_{12}(x) &= C e^{-(x+7)^2}. \end{aligned} \quad (3)$$

Here,  $A = 0.03$  and  $B = 1.6$ , and all units are in a.u. The diabatic coupling  $C$  dictates the interaction between diabatic surfaces, and we plot the diabatic Hamiltonian in Fig. 2(b) for a range of diabatic couplings.

The physics of the model problem in Eq. (3) is fairly straightforward. We imagine the particle incoming from the left, *now on the excited adiabatic surface*. The particle passes through one avoided crossing, which yields components of the electronic wavefunction on both the ground and excited states; one can think of this process as a Landau-Zener crossing. As one might expect, for transmission FSSH matches the exact answers accurately (data not shown). For  $k_{inc} < 22$  a.u., the wave packet on the upper surface will reflect at  $\sim x = 0$  and at this point the two wave packets (upper reflected, lower transmitted) must separate, or decohere. Afterwards, the reflected wave packet will pass through the avoided crossing for a second time going in the opposite direction. If the electronic amplitude does not correspond to the correct adiabatic state – and it usually will not according to the traditional FSSH algorithm – then we expect to see artificial oscillations in the reflection branching ratios,<sup>42,43</sup> which would be a “signature” of the decoherence failures of FSSH. Note there are no traps or resonances in this model problem, so the exact branching ratios will not oscillate and this model problem gives us a very simple system to understand FSSH dynamics when wave packets separate on different surfaces.

In Fig. 4, we show branching ratios for reflection as calculated by FSSH and exact quantum dynamics, both for plane waves and wave packets. Just as in Fig. 1, we find artificial oscillations in the FSSH branching ratios prior to the smoothing process. Interestingly, the averaged FSSH values are fairly accurate for modeling the corresponding wave packet data for the case  $C = 0.01$ . In fact, with no other information, the agreement for  $C = 0.01$  would appear to be another example of Tully’s empirical result in Ref. 2, whereby the effects of decoherence can be approximated by averaging FSSH over a distribution of initial conditions. This suggestion is illusory, however, because it applies only to one particular choice of the  $C$  parameter. When simulations are

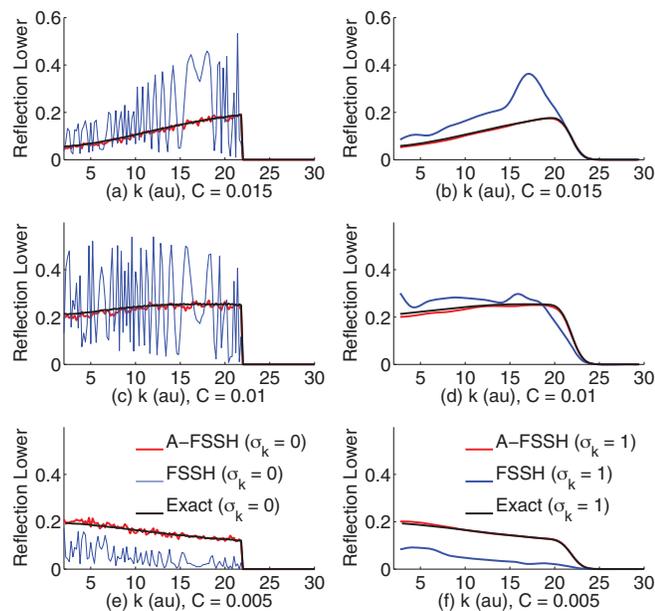


FIG. 4. Reflection probabilities onto the lowest adiabatic state for the model problem in Eq. (3). The potential energy surfaces are shown in Fig. 2(b) and we imagine the particle incoming on the upper adiabatic surface from the left. The raw FSSH results show unphysical oscillations compared with the plane wave calculations (on the left—(a), (c), (e)). For the case  $C = 0.01$ , the averaged FSSH results match the exact wave packet results pretty well (d), but this rough agreement is not true for either  $C = 0.015$  (b) or  $C = 0.005$  (f). Our recently developed A-FSSH algorithm, with a decoherence correction, performs very well in all cases.

performed on models with larger or smaller diabatic couplings ( $C = 0.015$ ,  $C = 0.005$ ), FSSH performs poorly. In fact, after testing many other values for the coupling strength  $C$ , we find that the averaging procedure is successful only for the fortuitous value of  $C = 0.01$ . This example demonstrates that, in all but a few cases, the FSSH algorithm's failure to take decoherence into account cannot be corrected by averaging over initial conditions.

### III. DISCUSSION

#### A. Fortuitous cases

Figure 4 shows that averaging FSSH trajectories over a swarm of initial conditions does not correct for decoherence except in very specific cases. Now, admittedly, neither FSSH (nor A-FSSH) allows for any quantum-mechanical effects for the nuclear motion, e.g., transient tunneling into the barrier, so one cannot expect perfect agreement between surface-hopping and exact results. Nevertheless, one can ask: what are those specific cases, such as  $C = .01$  in Fig. 4(d) for which averaging appears to qualitatively capture the effects of decoherence? To draw a complete picture, we will now identify why averaging FSSH trajectories over initial conditions is occasionally successful and in the process, we will better understand the data in Fig. 1(c) (Ref. 2) and Fig. 4(d).

Consider a particle with  $k_{inc} < 22$  moving on the upper adiabatic in Fig. 2(b) immediately after it reflects at  $x = 0$ . The exact decoherent result would require that the electronic state of the particle should be  $(0,1)$ , since it should collapse onto the upper electronic state. But because there is no decoherence in FSSH, the particle will instead carry an incor-

rect electronic amplitude,  $(\alpha, \beta)$ , as it moves back towards the avoided crossing at  $x = -7$ . To explore the ramifications of starting with an incorrect electronic amplitude, we have simulated FSSH dynamics starting with different values of  $|\alpha|^2$  and  $|\beta|^2$  for a swarm of trajectories all beginning on the upper surface and moving leftward from an initial position of  $x = -2$ . This is equivalent to calculating branching ratios for the model in Fig. 2(a), except that we use an initial electronic state  $\psi_0 = (\alpha, \beta)$  rather than  $\psi_0 = (0, 1)$ . In Fig. 5, we plot the branching ratios for transmission on the lower surface as a function of  $|\beta|^2$ , for a particle initialized with an incorrect electronic amplitude  $(\alpha, \beta)$  rather than the correct decohered amplitude  $(0, 1)$ .

In addition to examining the dependence of the electronic dynamics on electronic state populations  $|\alpha|^2$  and  $|\beta|^2$ , we need to also consider the effects of the phase. The wavefunction components  $(\alpha, \beta)$  will build up a relative phase due to the time spent between the initial traversing of the curve crossing and the second traversing of the curve crossing after reflection. In Fig. 5(d), we set  $\alpha, \beta$  to be real numbers. As expected from Fig. 4, we find large oscillations in the resulting transmission values, and this is true whether we choose  $C = 0.005, 0.01$ , or  $0.015$ . These oscillations are not purely sinusoidal, and they come with kinks reminiscent of the non-sinusoidal behavior found in Fig. 4 in the range  $k_{inc} \in [16, 18]$ . In Figs. 5(a)–5(c), we calculate transmission values for  $\alpha$  real and  $\beta = |\beta|e^{i\eta}$ , where we average over the initial phase  $\eta$ , chosen from a uniform distribution  $\eta \in [0, 2\pi]$ . Although the averaging removes the oscillations seen in Fig. 5(d), the branching ratios do still depend on

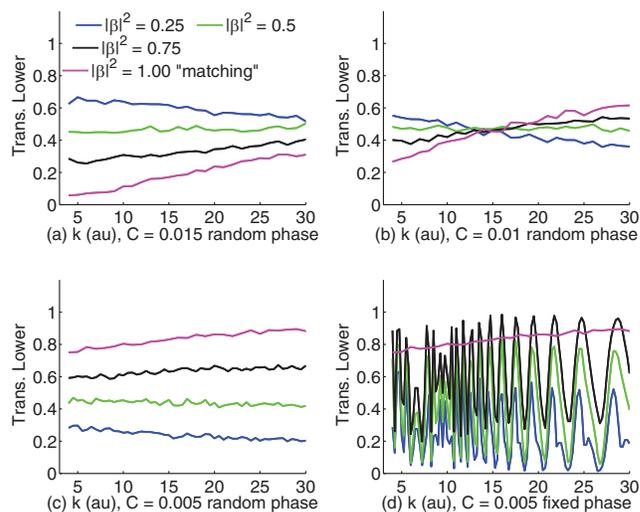


FIG. 5. Probabilities for transmission onto the lower surface after hopping down from the upper surface during an avoided crossing. See Fig. 2(a). Here, we measure this probability as a function of  $k_{inc}$  and the initial electronic amplitude,  $(\alpha, \beta)$ , where  $\alpha$  denotes the electronic amplitude on the lower adiabatic and  $\beta$  denotes the component on the upper adiabatic. Normally, we should set  $\alpha = 0$  and  $|\beta| = 1$ , so that the electronic amplitude matches the active FSSH surface. However, because it lacks decoherence, FSSH often at times has an inconsistent electronic amplitude. In order to address the implications of having such a wrong (overly coherent) amplitude, we plot branching ratios here for the cases  $|\beta|^2 = 0.25, 0.5, 0.75, 1$ . In (d), we fix  $\alpha, \beta$  as real numbers, but in [(a)–(c)], we sample from an initial distribution where there is a random phase  $\eta$  between  $\alpha$  and  $\beta$ , chosen randomly  $\eta \in [0, 2\pi]$ . See text.

$|\beta|^2$ . Recall that the properly decohered result requires that the reflected wavefunction should be  $|\alpha|^2 = 0$ ,  $|\beta|^2 = 1.0$ . As might be expected, the farther  $|\beta|^2$  is from 1.0, the more distorted the resulting branching ratios are.

The results in Fig. 5 are crucial for understanding how, in Fig. 4, one can sometimes average FSSH branching ratios over  $k_{inc}$  and fortuitously achieve greater accuracy. As noted above, the amount of time that passes between a particle's first and second traversals of the avoided crossing depends on its momentum. The difference in the elapsed time between the avoided crossings results in different relative phases between upper and lower electronic state components. Therefore, for the reflection branching ratios in this problem, *averaging over initial momentum implies averaging over a relative phase between  $\alpha$  and  $\beta$* . Because the correct, decoherent answer requires the amplitude of  $\alpha$  to be exactly 0 and, hence, have no phase relative to  $\beta$ , this averaging is certainly more accurate than choosing some fixed random phase. That being said, there is no guarantee as to how FSSH would behave if the particle were to undergo yet another crossing event. Moreover, even with only two avoided crossing events, the FSSH results need not be accurate because the final answers do depend on  $|\beta|^2$  which will not be substantially corrected by averaging over initial momenta. One can then ask: in what cases would we expect averaging, i.e., stochastic sampling, to help correct for decoherence?

*A priori*, we can identify only one particular case where stochastic sampling of initial conditions will be sufficient for describing decoherence. Let us imagine that the net effect of a particle passing through some avoided crossing with momentum  $k$  is to apply some unitary transformation  $U(k)$  to the electronic state of the particle. Let us further assume that the unitary operator happens to perfectly mix the two electronic components, i.e.,

$$U(k) \equiv \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & -e^{i(\theta+\gamma)}/\sqrt{2} \\ e^{-i\theta}/\sqrt{2} & e^{i\gamma}/\sqrt{2} \end{pmatrix}, \quad (4)$$

so that  $|U_{11}| = |U_{21}| = |U_{12}| = |U_{22}| = 1/\sqrt{2}$ . For an incoming particle with an electronic amplitude  $(\alpha, \beta \exp(i\eta))$ , the outgoing state is  $(\alpha - \beta \exp(i(\eta + \theta + \gamma)), \alpha \exp(-i\theta) + \beta \exp(i(\eta + \gamma)))/\sqrt{2}$ . If we now calculate the populations of the two electronic states and average over all relative phases  $\eta$ , we obtain populations of  $(1/2, 1/2)$  regardless of the values of  $\alpha$ ,  $\beta$ , or  $\theta$ . This same result is also obtained when the incoming state has been correctly decohered, i.e., it is  $(0, 1)$ . Thus, for the particular case of perfect mixing the correct state, populations of  $(1/2, 1/2)$  are always obtained through averaging over the relative phase  $\eta$ , regardless of the particular value of  $\beta$ . For other transformations  $U'(k)$ , however, we would find no such a result.

With this background in mind, consider again the case  $C = 0.01$  in Fig. 4, where averaging provided a good approximation to decoherence effects. This regime corresponds exactly to the crossover between predominantly diabatic and adiabatic behavior such that traversing the curve crossing leads to “perfect mixing” between the upper and lower electronic states. When the particle on the upper state is reflected and traverses the curve crossing a second time, one finds re-

flexion branching ratios of  $\sim 1:1$  between the upper and lower states. Thus, averaging FSSH results works so well in Fig. 4 *only because of a fortuitous choice of Hamiltonian parameters*. Further evidence is provided by Fig. 5(b). Here, one notices that for  $k < 30$ , all of the curves are fairly close together: one predicts transmission onto the upper and lower curves usually between 40–60%. Moreover, one sees (remarkably) that near  $k = 15$ , all of the incoming wave packets predict 50% transmission ratios on both surfaces. In other words, 50% of the probability will end up on the upper and lower surfaces regardless of the initial electronic state of the wave packet. Again, this is true precisely because at  $k = 15$ , the curve crossing implements “perfect mixing” of the electronic states. Below or above this  $k$  value, perfect mixing does not occur and the outgoing state populations do depend on the incoming value of  $\beta$ . Taken together, this evidence strongly suggests that decoherence cannot be accounted for by averaging FSSH results, in general.

Finally, we can ask whether this “perfect mixing” phenomena has any relevance to the success of stochastic sampling when applied to Tully problem #3 in Fig. 1. If we follow the dynamics on each incoming surface after passing through the region of derivative coupling, we find the following:

$k_{inc}$	$ U_{11}  =  U_{22} $	$ U_{12}  =  U_{21} $
10	0.83	0.55
15	0.79	0.60
20	0.77	0.63
25	0.76	0.64

Although these values do not correspond exactly to “perfect mixing,” whereby we need  $|U_{ij}| = 1/\sqrt{2} \approx 0.707$  in Eq. (4), the transformations are close. This result explains the coincidental agreement between the exact wave packet and averaged FSSH results in Fig. 1(c).

## B. The augmented FSSH decoherence correction

Because standard FSSH requires a decoherence correction, we have recently introduced an A-FSSH algorithm,<sup>42</sup> which addresses the decoherence problem while avoiding the spawning problem.<sup>44</sup> The A-FSSH algorithm uses a moment expansion<sup>45–47</sup> to determine when to collapse the electronic wavefunction during a FSSH trajectory. The essential assumption behind the A-FSSH algorithm is that, as a classical particle bifurcates on different potential energy surfaces, one can define an “intrinsic” width so that the collapse rate becomes roughly the difference in potential energy divided by  $\hbar$ . Clearly, more rigorous and more expensive schemes for decoherence exist in the literature based on initial value representations. We have also recently introduced an approach for implementing decoherence based on the initial width of the wave packet at time zero,<sup>48</sup> which has also proven fruitful. Nevertheless, for all problems studied thus far, our A-FSSH algorithm gives a meaningful correction to FSSH dynamics, and with very moderate cost – only 2–4 times

more than traditional FSSH for problems with two electronic states.<sup>49</sup>

As applied to the Hamiltonian in Eq. (3), A-FSSH predicts that for all trajectories that are reflected on the upper excited state, one should collapse the wavefunction during the reflection process, thus enforcing decoherence within a FSSH framework. From Fig. 4, one observes that collapsing the wavefunction leads to quantitatively accurate results for reflection branching ratios. As applied to the Hamiltonian in Eq. (1), A-FSSH predicts that there should be some collapsing events while the particle is trapped in the resonant state. As a result, the A-FSSH results lose some of the resonance peaks we would predict for plane waves in Fig. 3(a), but we do find the correct ratio of reflection for a narrow enough (classical) wave packet in Figs. 3(b) and 3(c). Lastly, when applied to Tully's model problem #3, we showed in Ref. 42, that the A-FSSH algorithm again performs very well. Altogether, this strongly suggests A-FSSH is an inexpensive and meaningful improvement upon the traditional FSSH algorithm.

#### IV. TWO-DIMENSIONAL CONFIRMATION

Before concluding, we now demonstrate that the results above are general, and, in particular, that our conclusions apply in more than one dimension. Consider the following two-dimensional Hamiltonian, which extends our previous model:

$$\begin{aligned} V_{11}(x, y) &= A \tanh(B(x + 7)) \\ &\quad + 2A \tanh(Bx + 2.2 \cos(y + 1.33)) + 2A, \\ V_{22}(x, y) &= -A \tanh(B(x + 7)), \\ V_{12}(x, y) &= C e^{-(x+7)^2} (2 + \cos(0.8y + 0.46)). \end{aligned} \quad (5)$$

Here,  $A, B$  are as in Eq. (3) and we choose  $C = 0.0025$  or  $C = 0.004$ . A contour of this potential is shown in Fig. 6. We imagine an incoming Gaussian wave packet on the upper surface, with  $(k_x^{initial}, k_y^{initial}) = (15, 5)$  and  $(x^{initial}, y^{initial})$  centered either at  $(-15, -5)$  or at  $(-15, -4)$ . The widths of the Gaussians in real space are chosen as  $\sigma_{x,y}$ , where

$$|\Psi_{tot}(x, y, t = 0)\rangle = \frac{1}{2\pi\sigma_x\sigma_y} \exp\left(-\frac{(x - x^{initial})^2}{4\sigma_x^2} - \frac{(y - y^{initial})^2}{4\sigma_y^2} + ik_x^{initial}x + ik_y^{initial}y\right) |\Phi_{el}^{upper}\rangle,$$

and for a Gaussian wavefunction, one always finds:  $\sigma_x\sigma_{p_x} = \sigma_y\sigma_{p_y} = 1/2$ . After the initial avoided crossing around  $x = -7$ , if the wave packet is on the lower surface, it will transmit ( $x \rightarrow +\infty$ ); otherwise, it will scatter back ( $x \rightarrow -\infty$ ). The important feature of this two-dimensional model is that it is highly non-separable; the dynamics will depend on the second nuclear degree of freedom in some highly non-trivial way.

Our computational results are shown in Table I. As in the one-dimensional case, averaging FSSH over initial conditions does not lead to the correct branching ratios. Instead, the correct branching ratios are found only if we both average over initial conditions and also apply a decoherence correction (e.g., the A-FSSH algorithm).

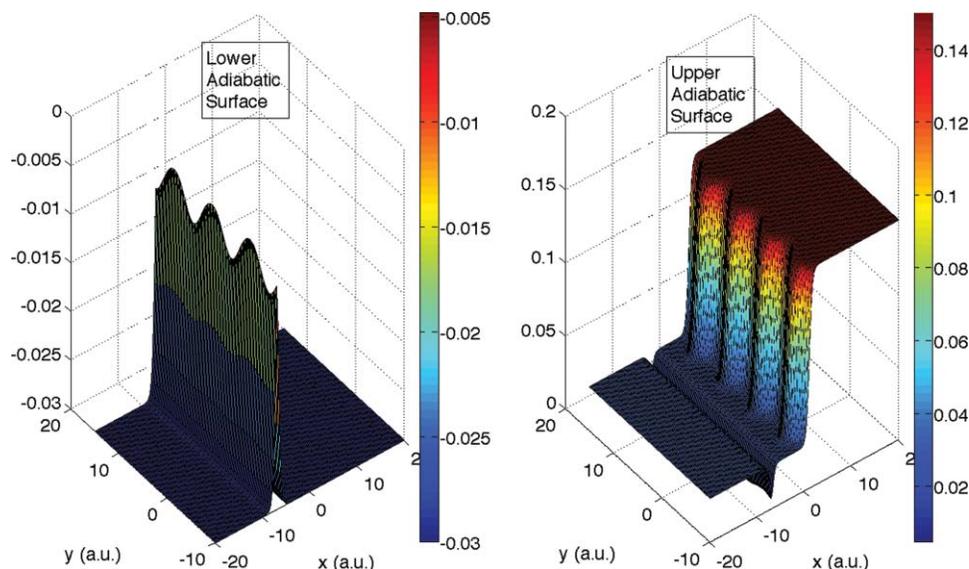


FIG. 6. Adiabatic energy contours for the Hamiltonian in Eq. (5). We use this two-dimensional model for testing the relationship between decoherence and averaging over initial conditions.

TABLE I. The probability to reflect ( $x \rightarrow -\infty$ ) on the lower surface according to exact quantum wave packet dynamics, FSSH, or A-FSSH. To obtain the best results possible, one must both (i) average over initial conditions to explore phase space in a meaningful way and (ii) use an algorithm with an explicit decoherence correction, e.g., A-FSSH, to account for wave packet separation. Neither (i) or (ii) is sufficient alone.

Starting position	Algorithm	Averaged over	Prob. refl.	Prob. refl.
		initial conditions $\sigma_x = \sigma_y = 1/2$	lower channel $C = 0.0025$ a.u.	lower channel $C = 0.004$ a.u.
(-15,5)	Exact	n/a	14%	19%
	FSSH	YES	5.7%	19%
		NO	9.4%	20%
	A-FSSH	YES	14%	18%
NO		14%	14%	
(-15, -4)	Exact	n/a	20%	25%
	FSSH	YES	8.7%	26%
		NO	20%	53%
	A-FSSH	YES	20%	25%
		NO	25%	35%

## V. SUMMARY

As applied to Tully-style surface hopping (FSSH), we have shown that (i) averaging over initial conditions does not yield a meaningful decoherence correction, and (ii) when wave packets decohere, any perceived improvement of results from averaging over initial conditions, e.g., as found in Ref. 2, is entirely fortuitous. In general, averaging over initial conditions in FSSH captures only the spread of a wave packet on a single potential energy surface. While this averaging is necessary, especially for scattering problems where branching ratios oscillate as a function of incoming energy, this averaging does not capture the physics of wave packet bifurcation on multiple surfaces. For a nonadiabatic problem with two regions of derivative coupling, averaging over initial conditions does imply averaging over a random relative phase between the two relevant electronic amplitudes. Nevertheless, while this phase-averaging may eliminate spurious oscillations, it will not usually yield accurate results if there is wave packet separation on different surfaces. Stochastic sampling in FSSH will be a satisfactory substitute for a decoherence correction only in those rare cases where the curve crossing can be well-described by a “perfect mixing” unitary transformation which leads to a 1:1 branching ratio between electronic populations. In the end, a good surface hopping model based on FSSH must both (i) average over initial conditions and (ii) implement an independent decoherence correction. Thus far, our recently introduced A-FSSH algorithm has performed well on all model problems, suggesting that decoherence can and should be treated both accurately and efficiently within the FSSH framework.

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